

Electrolyte Loss Mechanisms of Manually Activated Silver-Zinc Cells and Batteries

10 December 1996

Prepared by

L. H. THALLER and G. L. JUVINALL
Electronics Technology Center
Technology Operations

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245


19970527 024

Space Systems Group

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-93-C-0094 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by R. P. Frueholz Principal Director, Electronics Technology Center. Lt. Col. J. E. Gazur was the project officer.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

 for

Lt. Col. J. E. Gazur
SMC/SSG

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 10 December 1996		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE Electrolyte Loss Mechanisms of Manually Activated Silver-Zinc Cells and Batteries			5. FUNDING NUMBERS F04701-93-C-0094	
6. AUTHOR(S) L. H. Thaller and G. L. Juvinall				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Technology Operations El Segundo, CA 90245-4691			8. PERFORMING ORGANIZATION REPORT NUMBER TR-97(1494)-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Materiel Command 2430 E. El Segundo Boulevard Los Angeles Air Force Base, CA 90245			10. SPONSORING/MONITORING AGENCY REPORT NUMBER SMC-TR-97-11	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Silver-zinc batteries are used in applications where high energy density and high discharge rates are required. These batteries do not possess excellent cycle life characteristics, but designs are available that are capable of about a hundred charge-discharge cycles. These batteries are mostly used in the primary mode where they are not required to be recharged. Torpedoes, missiles of many different varieties, and all launch vehicles use silver-zinc batteries in sizes ranging from about one ampere-hour (A-h) to 250 A-h. For the launch vehicle applications discussed herein, batteries are assembled except for the introduction of electrolyte and carefully stored until they are called up for use. At that time, electrolyte is added as part of the overall activation process prior to installation on the vehicle. Once the cells are filled, reactions take place that can result in small amounts of electrolyte being expelled from them. There have been several recorded instances where electrolyte expulsion has resulted in the rejection of either that particular battery or the entire production lot of batteries that were felt to have a generic problem. An in-flight failure of a battery suggested that the problem resulted from the effects of small amounts of electrolyte forming an ionic conduction path inside the battery box. This report covers the results of examining the causes for the different kinds of problems within a cell that can result in the expulsion of small amounts of electrolyte.				
14. SUBJECT TERMS Silver-zinc, Electrolyte loss, Cell design			15. NUMBER OF PAGES 34	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

Contents

1.	Introduction	1
2.	Background	3
3.	Aspects of Silver-Zinc Cell Design and Manufacture.....	7
3.1	Cell Chemistry	7
3.2	Potassium Oxalate Crystals	7
3.3	Amalgamation of the Zinc Electrodes	8
3.4	Manufacture of Zinc Electrodes	8
3.5	Cell Design	9
4.	Battery Storage	11
5.	Battery Activation	13
6.	Flight Usage	17
7.	Static Model	19
8.	Results	23
9.	Conclusions	25
	References	27
	Appendix—Silver-Zinc HR-13 Cell Design Information.....	29

Figures

1. Details of the vent valve.....	3
2. Typical cell vacuum backfilling arrangement.....	13
3. Interior cell volume.....	20
4. Interior free volume.....	20
5. Electrolyte distribution.....	21

Table

1. Tolerance to Changes in Free Electrolyte Volumes of Several Cell Types	23
---------------------------------------------------------------------------------	----

1. Introduction

Silver-zinc batteries are used in applications where high energy density and high discharge rates are required. These batteries do not possess excellent cycle life characteristics, but designs are available that are capable of about a hundred charge-discharge cycles. These batteries are mostly used in the primary mode where they are not required to be recharged. Torpedoes, missiles of many different varieties, and all launch vehicles use silver-zinc batteries in sizes ranging from about one ampere-hour (A-h) to 250 A-h. For the launch vehicle applications discussed herein, batteries are assembled except for the introduction of electrolyte and carefully stored until they are called up for use. At that time, electrolyte is added as part of the overall activation process prior to installation on the vehicle. Once the cells are filled, reactions take place that can result in small amounts of electrolyte being expelled from them. There have been several recorded instances where electrolyte expulsion has resulted in the rejection of either that particular battery or the entire production lot of batteries that were felt to have a generic problem. An in-flight failure of a battery suggested that the problem resulted from the effects of small amounts of electrolyte forming an ionic conduction path inside the battery box. This report covers the results of examining the causes for the different kinds of problems within a cell that can result in the expulsion of small amounts of electrolyte.

2. Background

Silver-zinc cells used on launch vehicles are not hermetically sealed. Figure 1 shows how the vent valve and top assembly of a typical silver-zinc cell is constructed in an attempt to minimize the inadvertent loss of electrolyte. The function of the chimney is to prevent bulk liquid from reaching the vent valve in the event the cell or battery is inverted. These cells generally have very little electrolyte that is not held within the pores of the different internal components of the cell. This is generally referred to as "free" electrolyte. The vent valve is a threaded piece that is sealed by being seated against an O-ring located in a recessed groove at the top of the cell. A short piece of neoprene tubing fitted over the horizontal openings of the valve body seals the cell against the intrusion of air. When the internal cell pressure increases to the point where the rubber can be temporarily pushed away, the gases within the cell are released and the valve closes. The pressure at which the cell vents is set by the differential pressure across the rubber tube. This is generally in the range of 3 to 5 psi. With this type of construction, small amounts of electrolyte can be expelled from these cells between the time they are first filled and the time when the vehicle on which they are being used has completed its mission. The causes for this expulsion of electrolyte are varied. Over the years of use in this application, and based on experience with a variety of electrolyte-related issues, the following list of explanations has been assembled from several sources.

1. The amalgamation process had been improperly applied, which resulted in excessive hydrogen gassing within the zinc electrodes and consequent expulsion of electrolyte.
2. The normal evolution of hydrogen gas carried small droplets of electrolyte with it as it escaped out through the vent valve.

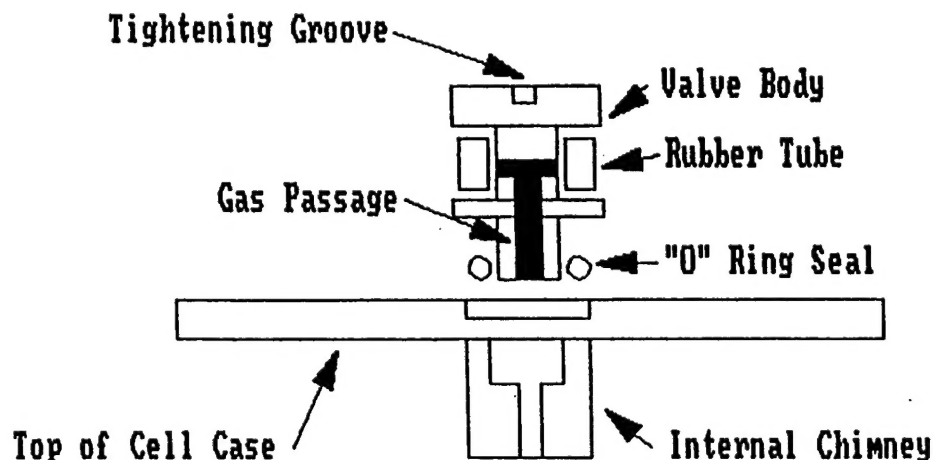


Figure 1. Details of the vent valve.

3. Improper sealing pressure applied to the O-ring located between the cell top and the bottom of the vent valve allowed hydrogen accompanied by droplets of electrolyte to escape from the base of the vent valve.
4. Overfilling of the cell in terms of the amount of electrolyte resulted in the expulsion of liquid.
5. Hydrogen bubbles generated during the first few hours following cell filling that did not disengage from the electrolyte formed a froth or foam that expelled liquid along with gas from the cells. (This is usually caused by surface-active contaminants within the cell.)
6. A cell design that had insufficient "head room" above the plate pack to accommodate the pushing out of electrolyte from the porous zinc plates by the hydrogen evolved during the reaction between potassium hydroxide and the fresh zinc-plate material.

In an actual battery application, the individual cells with vent valves that release at a pressure differential of 3 to 5 psi are placed within a battery box with a relief valve that vents at a differential pressure of 10 to 12 psi. The evolution of modest amounts of hydrogen from the cell vent valves is perfectly normal. The cells always contain a significant partial pressure of hydrogen gas. However, during flight, when the vehicle reaches high altitudes, it is then not uncommon for the battery to vent to the vacuum of space, and for the individual cells to release some hydrogen gas to the interior of the battery box.

Within the past several years, there have been several instances of excessive amounts of electrolyte being expelled from silver-zinc cells. These situations can be subdivided into what can be called spattering (cases 1, 2, and 3), frothing (case 5), and overflowing (cases 4 and 6). These have resulted in a suspected inflight battery failure as well as several ground failures prior to launch. These situations can be minimized by several procedures that are part of the activation process prior to installation onto the flight vehicle. This report addresses all of these issues.

One or more of the above-listed instances have been experienced within the recent past by each of the program offices using silver-zinc batteries aboard their vehicles. In support of these program offices, a MOIE-funded project developed a static model for these cells that carefully calculates the volumes of the components within a cell. Knowing the dimensions, apparent volumes, weights, and specific gravities of the assembly of parts making up the plate pack and electrode leads, along with the interior volume of the cell case and the volume of electrolyte added during the filling process, the tendency for a particular cell design to expel small amounts as per case 6 can be calculated. Comments related to the other known causes of electrolyte expulsion are addressed as well. Electrolyte expulsion is only one of a number of silver-zinc-related issues that are currently being compiled by individuals within Aerospace.

Once the spreadsheet-based model was developed, a review of the tendency to expel electrolyte from vented silver-zinc cells based on their cell design was carried out. As a result of analyzing four different cell types, a wide range of tolerance for accommodating changes in the volume of free electro-

lyte (electrolyte not contained within the porous components of the cell) has been noted. Cell designs that can accommodate only small amounts of free electrolyte within the cell represent a risk in terms of expelling electrolyte during the activation process, the wet stand period, or actual flight usage. This is of particular concern for battery designs where the individual cells are not fully potted within the battery box.

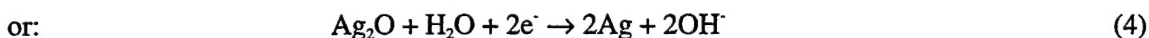
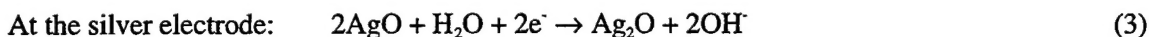
3. Aspects of Silver-Zinc Cell Design and Manufacture

3.1 Cell Chemistry

References 1, 2, and 3 are excellent resources when extended explanations and descriptions of the finer points of silver-zinc cell design, storage, and performance are required. The comments and equations presented in this section, by necessity, will be a very brief overview of some of the major factors influencing cell design.



Eq. (1) is often used to describe the overall reactions taking place within a cell during its discharge. High-surface-area zinc electrodes and electrochemically prepared silver oxide electrodes are physically separated using a multi-layer separator system. The electrolyte is a very concentrated solution of potassium hydroxide (typically 42 wt.% KOH). Unfortunately, this simplistic equation hides some very important processes that impact the design of a practical cell.



Eq. (2) suggests that hydroxide ions are consumed at the zinc electrode as soluble zincate ion is formed near the surface. As long as soluble zincate ion is formed rather than insoluble forms of discharged zinc, then the electrode will continue to deliver large amounts of current. If the rate of diffusion of hydroxide ions is not rapid enough to be able to replenish those consumed in the zincate reaction, the internal resistance of the cell will rise very rapidly, and the cell will no longer be able to operate at high current densities. The amount of electrolyte and the concentration of potassium hydroxide required for the cell's intended application is determined by the mass transport and the super-saturation limits of the zincate ion under the conditions under which the cell is being discharged and the duration over which the discharge is required. Foundational studies carried out at Naval Research Laboratory in the late 1940s were instrumental in helping manufacturers establish their own design codes in terms of surface area, porosity, and electrolyte quantities.⁴

3.2 Potassium Oxalate Crystals

Besides the electrolyte requirements being dictated by current density (mA/cm^2) and capacity (mAh/cm^2), there are other factors to be considered as well. The amount of electrolyte affects the rate of growth of potassium oxalate crystals that form within the layers of cellulosic separator material. These crystals, which result from the interaction of potassium hydroxide with cellophane, can lead to

tears in the separator during the rigors of launch. Very often this results in potentially dangerous short circuits within the cell. The concentration of electrolyte affects the rate of formation of potassium oxalate as well as the gassing rate at the zinc electrodes as described in Eq. (5).



3.3 Amalgamation of the Zinc Electrodes

A major factor that must be considered in the design of silver-zinc cells is the rate of gas evolution. High rates of gas evolution can result in unacceptable amounts of electrolyte expulsion even when other essential cell design features, such as adequate free volume, reliable pressure relief valves, etc., have been provided.

Zinc is an amphoteric metal, and thus is thermodynamically unstable in aqueous potassium hydroxide. The reaction of the zinc with aqueous potassium hydroxide solution is described in Eq. (5). In practice, the rate of hydrogen evolution is reduced by amalgamation of the zinc electrodes and by stringent quality control measures. The addition of mercury to the zinc electrodes (amalgamation) raises the hydrogen overvoltage and effectively inhibits the evolution of hydrogen by "local action," which is essentially corrosion of the zinc. Normally, the mercury constitutes about 1% to 2% by weight of the finished anode. Increasing the mercury content from 1% to 2% decreases the rate of evolution of hydrogen by a factor of 10 (Ref. 5).

The rationale for adding mercury to the zinc electrodes is as follows: Overvoltage may be defined as the additional voltage above the reversible emf of an electrochemical reaction that must be impressed to cause the reaction to proceed at an appreciable rate. In other words, additional energy is required to enable the reaction to proceed readily. The total overvoltage is the sum of individual overvoltages at the cathode and anode. Since the reversible emf of the reaction is a direct measure of the Gibbs free energy of the reaction, it may be seen that raising the hydrogen overvoltage by any means will reduce the ability to produce gaseous hydrogen. Thus, one would expect mercury to be effective in suppressing hydrogen evolution from the zinc electrode. In general, the soft metals of low melting point, such as tin, cadmium, and mercury, show the highest hydrogen overvoltages.⁷ The transition metals and noble metals typically exhibit low hydrogen overvoltages.

3.4 Manufacture of Zinc Electrodes

A brief discussion of the manufacture of zinc electrodes is perhaps in order. Zinc electrodes for secondary silver-zinc cells are typically constructed by a pasting process. Zinc oxide, mercuric oxide, and a binder are mixed with water to form a slurry. The slurry is uniformly applied to a metal substrate (current collector) and pressed or rolled. The finished electrodes are then placed in a forming bath and electrochemically reduced to amalgamated metallic zinc. Cell designs based upon the use of mercuric sulfide have also been developed and tested.⁶ Through control of the pressing process, as well as current density, temperature, and potassium hydroxide concentration in the electroforming bath, the manufacturer is able to provide electrodes of the correct thickness and porosity.

The negative electrodes for primary silver-zinc cells are frequently made by an entirely different process. Porous or "spongy" zinc is electrochemically plated on a metallic substrate. After rinsing and drying, the electrodes are pressed or rolled to the desired thickness and final porosity. Amalgamation is then effected by immersion in an aqueous solution of a mercuric salt, followed by drying in a carefully controlled oven. The mercury is chemically reduced by the zinc and thus amalgamates the electrode. The manufacturers' proprietary processes control the temperature, current density, zinc-ion concentration, etc., so that the spongy zinc plates will have the correct porosity when rolled to the specified thickness. The amalgamation process is controlled by the concentration of the mercury salt and the temperature and residence time in the drying oven. The electrodeposited electrodes can be expected to evolve gas more vigorously than the pasted electroformed plates. Depending on the effectiveness of the amalgamation technique, there will still be small amounts of hydrogen released during the first several hours following the introduction of electrolyte. Under normal conditions, the rate of hydrogen evolution decays rapidly with time as the most active surface sites are oxidized. The purpose of the vent valve, as described earlier, is to release this gas as it builds up. As seen below, the hydrogen formed at and within the zinc electrode does not always completely disengage itself from the electrodes. It can be trapped within the interior of the porous structure and expel some of the electrolyte.

The quality control measures that bear on the rate of gassing involve the exclusion of metallic impurities, which effectively decrease the hydrogen overvoltage. As previously noted, Ref. 7 contains data from which it may be seen that mercury, cadmium, and tin have high hydrogen overvoltages. Conversely, the transition metals and noble metals have low overvoltages and must be excluded from the cells.

The quality control procedures must also be directed to the elimination of various organic compounds in the cell. Certain organic compounds, by altering the surface tension of the electrolyte, can induce foaming, which, in turn, can result in the expulsion of significant quantities of electrolyte. The organic compounds can enter the cell via contaminated components or be introduced during the manufacturing processes. Glycerol is normally used in cellophane as a plasticizer; however, the presence of glycerol can induce foaming and expulsion of electrolyte. In the cell environment, oxidation of the alcohol can proceed to the aldehyde and ultimately to the acid. A saponification reaction with the potassium hydroxide will then form a soap-like material that functions as a surfactant. Cellophane intended for separators in silver-zinc cells is procured without glycerol.

Organic compounds can also be inadvertently introduced during routine manufacturing procedures. In fact, compressed air used to agitate electrochemical formation baths has been known to contain compressor oil, which induced foaming.

3.5 Cell Design

Cells are, of course, designed so that excessive amounts of electrolyte will not be expelled. However, many of the current cell types were originally designed 20 or 30 years ago. Since that time, there has been an effort to extend the wet stand time from 15 days (for the very short wet stand limits associated with batteries using cells with only a few layers of separator) to up to 90 days for some requalified cell types. It is well known that extra layers of cellophane separator material can increase the wet stand time, but at the expense of an increased internal resistance. The addition of more electrolyte is

another method used to increase the wet stand time since it retards the formation of oxalate crystals mentioned above. For these reasons, the net free volumes within some of these designs have gotten smaller. One manufacturer redesigned the cell housing by shortening the protrusion length of the chimney to provide more free volume above the cell pack. Cell designs that may pose a problem in terms of expelling bulk electrolyte (overflowing) are ones where the net free volume within the cell following electrolyte addition is less than the interior volume of the zinc plates. This guideline is suggested since the solution of potassium hydroxide used as the electrolyte is known to react chemically with fresh zinc surfaces to produce hydrogen gas, which can push electrolyte out into the free volume of the cell.

4. Battery Storage

When completed batteries are delivered to the launch facility by the manufacturer, they are carefully stored in refrigerators to reduce the rate of the decomposition of the fully charged silver peroxide to silver monoxide and oxygen. The Gibbs free energy of reaction, Eq. (6), favors the spontaneous decomposition of silver peroxide. Reference 8 provides data that indicate that silver peroxide is 50% converted to silver monoxide in 98 h at 100°C. The data were obtained from constant-temperature thermograms of electrochemically prepared silver peroxide. Certain contaminants and manufacturing processes result in different decomposition rates for this material.



In a completely sealed cell, it is possible for the released oxygen to chemically discharge the equivalent amount of zinc from adjacent anode plates. The major effect is passivation of the zinc plate. Intruding oxygen can chemically discharge zinc as well but disproportionately to the amount of silver peroxide. Since the capacity of the silver electrodes is less than that of the zinc electrodes, this capacity loss is usually not noted. Individual cells should be tightly sealed during storage using the plugs provided by the manufacturers that are tightened against the O-ring located in the cell cover.

5. Battery Activation

Battery activation begins with the addition of measured amounts of potassium hydroxide solution into the group of cells contained in the battery. These solutions of concentrated potassium hydroxide are supplied in individual bottles by the battery manufacturer. The individual cells within a battery are typically filled (Figure 2) all at once by first creating a vacuum within the cells and then allowing the premeasured amounts of electrolyte to be sucked into them. To be complete, Figure 2 should show about 20 individual reservoirs and tubes connected to 20 separate cells. The greater the degree of vacuum that is established within the cells prior to the admission of electrolyte, the smaller will be the pore sizes of the components within the cells that will be filled with electrolyte. Depending on the contractor, several different filling procedures, degrees of vacuum, reapplications of vacuum (called

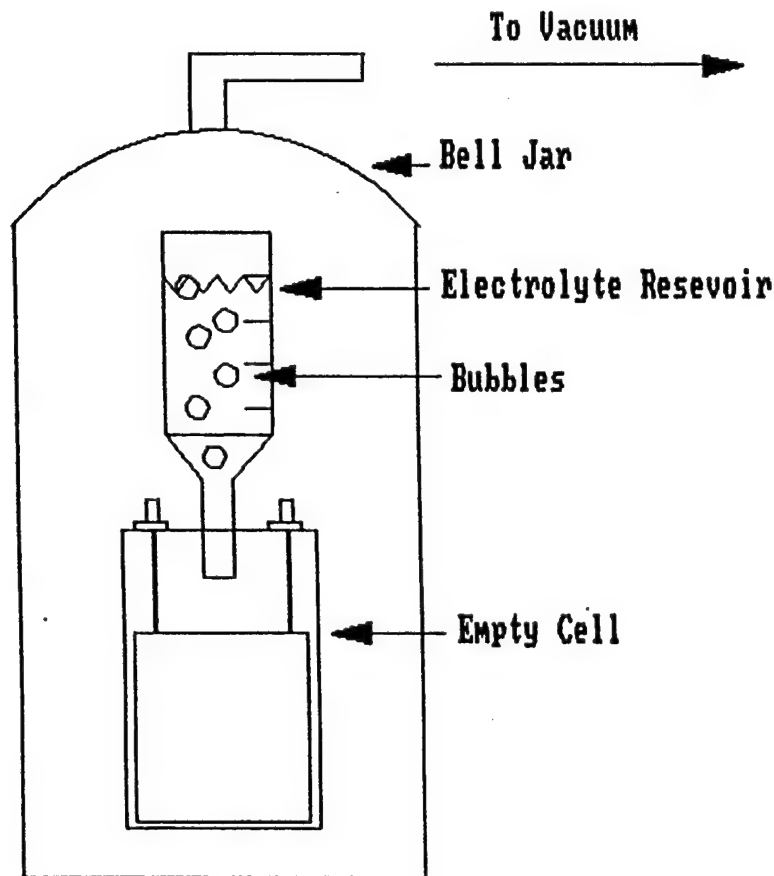


Figure 2. Typical cell vacuum backfilling arrangement.

redistribution steps), and waiting periods between steps are practiced. It is during the activation process that many different problems can arise that act to screen out batteries that may not be flight-worthy.

Once the individual cells are filled with their allotted amount of electrolyte, using the filling apparatus as described in the preceding paragraph, the electrolyte is allowed to soak into the porous cell components for up to several days before proceeding onto the next step in the activation process. The cellophane slowly swells as it absorbs electrolyte, and the newly exposed zinc plate material reacts with the electrolyte to form hydrogen. During the first few hours, the reactivity of the zinc is highest. The tubes of the filling apparatus are left in place so that the electrolyte that is expelled during the activation process can be quantitatively reintroduced into the cell during the redistribution steps that follow. The highly porous, woven and nonwoven portions of the separator system absorb electrolyte very quickly, but the multiple layers of cellophane require longer periods of time.

The degree of vacuum applied to the cell during the filling process will determine the minimum pore size into which the electrolyte will be forced. Capillary forces can be very strong, but it is very difficult to force the electrolyte into the smallest of the electrode pores. It is during the first few hours following activation that problems relating to (1) improper or insufficient mercury content in the zinc plate, (b) the presence of impurities that reduce the hydrogen overvoltage protection provided by the mercury content, or (3) the presence of saponifiable organic materials in the separator become evident.

Different manufacturers use their own preferred methods to amalgamate the zinc electrodes. Poorly amalgamated plates show high rates of hydrogen evolution that persist for longer times than typically seen. Certain metallic impurities can impact the gassing characteristics of zinc electrodes by altering the effects of the amalgamation process. Only rarely have organics been responsible for creating soap-like bubbles in silver-zinc cells. Under these conditions, hydrogen bubbles could not disengage properly, and a mixture of gas and bubbles exited the cell following activation with electrolyte. In the process of making the rolls of woven and nonwoven nylon material, oils are used to lubricate the rollers. With the cellulosic material, it is normal to produce it with large amounts of glycerol incorporated into its structure to give it the desired texture required in its main usage as a wrapping material. In the presence of the potassium hydroxide used as the electrolyte, these substances react to form compounds that makes the electrolyte foam during the release of small hydrogen bubbles.

Following electrolyte addition, soak time, and reapplication of the vacuum back-filling step(s), the battery is ready to continue in the activation procedure. At this point, the filling tubes connecting the cells to the filling apparatus are removed, and the pressure relief valves are screwed into the cell caps. For cell designs that do not use relief valves, pieces of open cell foam used as mist catchers are placed in the external portion of the filling chimney. Then, any spilled electrolyte is carefully wiped away from the cell tops. The individual cell voltages are measured and recorded. Out-of-family cells, as well as cells containing low-level short circuits, can be detected prior to the battery being "top charged." The charging step restores the capacity lost during dry storage, and the cell-to-cell balance within the battery can be verified. Batteries are charged per the manufacturer's recommendation until the first cell reaches the cutoff voltage. Low-level cell shorting has been experienced on rare occasions during this step in cases where (1) the cells were charged beyond the maximum recommended cut off voltage (~ 2.05 V at C/20), or (2) the electrolyte level was too high, permitting a zinc dendrite

to bridge over the tops of the separators until it touched one of the silver electrodes. Following a series of voltage checks and load tests, the battery is ready to be installed onto the launch vehicle. Under certain circumstances, about one-third of the battery's capacity is removed by a controlled discharge. This procedure results in a more stable voltage during the subsequent discharge of the battery during its mission. The batteries are then referred to as being in the monoxide state. Batteries are normally discharged to the monoxide state when they are intended for use in high-rate pulse applications.

Silver-zinc batteries experience several time-related degradation modes that place limits to the number of days between the time the battery is activated and the time the battery is no longer considered to be flightworthy. At the time electrolyte is first introduced into the cells, the clock that measures the permissible wet stand time is started. Each battery type is qualified to a certain permissible wet stand time. It is typically 15 days, or 30 days, or 45 days, etc. The silver oxide used as the active material in the positive electrodes is a very strong oxidizing agent and is partially soluble in the electrolyte. If it were to diffuse over to the zinc electrode, it would react with the zinc, leaving a small site of metallic silver on the zinc plate. This reduces the hydrogen overvoltage protection provided by the amalgamation process, and excess gassing takes place. The diffusion problem is reduced by using multiple layers of cellophane. The cellophane reacts with the silver ions before they reach the zinc electrode. The additional layers of cellophane result in a higher internal cell resistance and require longer soak times. A more significant time-related cellophane degradation mode is the formation of potassium oxalate crystals. These crystals form between the layers of cellophane and can puncture these thin layers of cellophane, resulting in the early onset of internal short circuits. During the qualification program to validate the wet stand limits for a particular cell design, the shock and vibration requirements are validated following the wet stand period. It is at this point that the largest potassium oxalate crystals will be present. Damage to the cell's separator system during the rigors of shock and vibration are most likely to occur.

6. Flight Usage

Once installed on the launch vehicle or upper stage, voltages are usually only available at the battery level. Upper and lower limits to battery voltage (red lines) are set to minimize the probability of launching a battery containing a defective cell. The voltage and current tests described in the preceding paragraphs screen out most of the out-of-spec batteries. Occasionally, launches experience inflight anomalies that can be attributed to the battery. The abrupt loss of about 1.5 V suggests that a cell has experienced a severe internal short circuit. The loss of more than this suggests that a more significant shorting path has developed that can reduce the bus voltage below the bus cutoff limit. An inflight failure that reduced the bus voltage below its lower cutoff was attributed to electrolyte being expelled from one or more cells through the vent valve. The electrolyte allowed an ionic shorting path between one or more of the cell terminals and grounded battery box. Through a succession of events, the shorting path evolved into a low-impedance carbon track to the spacecraft ground. In a matter of minutes, the high-current shunt path dropped the bus voltage to below its low-voltage limit, and this portion of the power system was taken off line. A static model for silver-zinc cells was developed in an attempt to review the tolerance of different cell designs to expelling electrolyte during the course of their operation.

7. Static Model

The model to be described here carefully accounts for all the components within a cell. These include electrodes, substrates, wire or foil leads, the separator system, etc. By determining the porosities and knowing the interior dimensions of the cell case and the amount of electrolyte added during activation, the tendency for a particular cell design to expel electrolyte by overflowing can be estimated.

Starting with a completely empty cell case (Figure 3a), the wasted head space due to the protrusion of the vent chimney into the upper part of the cell is subtracted to determine the cell's net free volume (Figure 3b). This volume is available for the dry cell components, the electrolyte, and the gaseous components. By calculating the volumes of the dry components and subtracting this volume from the net free volume, the gross interior free volume (Figure 4a) is calculated. This remaining volume is available for electrolyte and gas. The gross interior free volume, as determined from measuring the volumes of all the components of the plate pack, was double checked by using another cell and a different method. This second cell was connected to a calibrated volume at an accurately known gas pressure. By accurately measuring the pressures before and after admitting some of the gas from the calibrated volume into the cell, its gross free volume could be calculated using ideal gas laws. The volumes determined by these two methods agreed to within a few percentage points. A value of about 77 cm^3 was calculated by adding up all the internal cell components and a value of 75 cm^3 was determined using the gas transfer technique. Once the electrolyte is added, the remaining unoccupied volume (by solids or liquids) is called the net interior free volume (Figure 4b). The electrolyte, by virtue of the vacuum back filling process, is mostly drawn into the porous cell components. These include the electrodes and the different separator components. The cellophane absorbs considerable amounts of electrolyte as it expands. This remaining volume is also occupied by gases that are either trapped inside the porous cell components or occupy space outside these components. The amount of "free" electrolyte (the volume not contained within any of the porous components) depends primarily on the percentage of the zinc electrode pores that are filled with electrolyte. This free electrolyte must fit in those portions of the cell's net free volume that are outside of the porous components and are below the bottom of the chimney that protrudes down into the interior of the cell. Due to the possibility that some of the hydrogen gas remains trapped within the zinc electrodes, it cannot be determined what percentage of the porous volume of the zinc electrodes will contain electrolyte and what percentage will contain hydrogen. As described in the section on activation, different procedures are available to minimize this situation. Figure 5 depicts the general range of this situation. Depending on the value for the net interior free volume and the percentage of zinc electrode volume occupied by gases, a situation can take place where electrolyte is actually forced out of the vent valve. This, of course, is extremely undesirable.

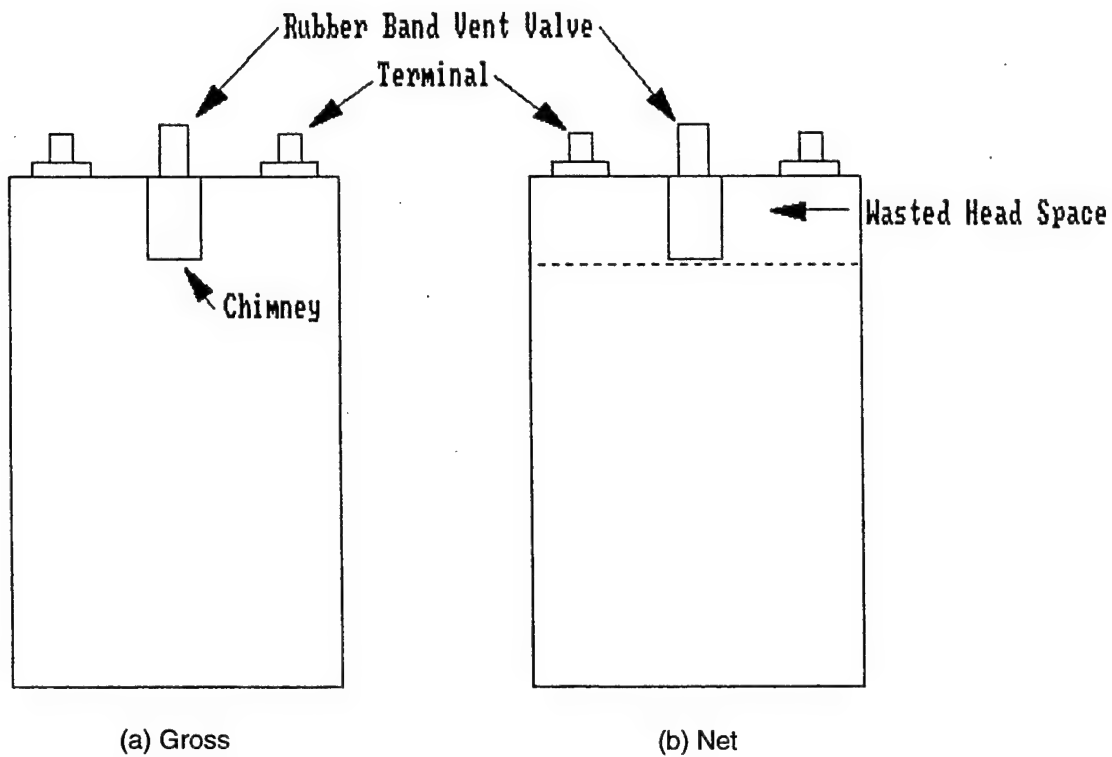


Figure 3. Interior cell volume.

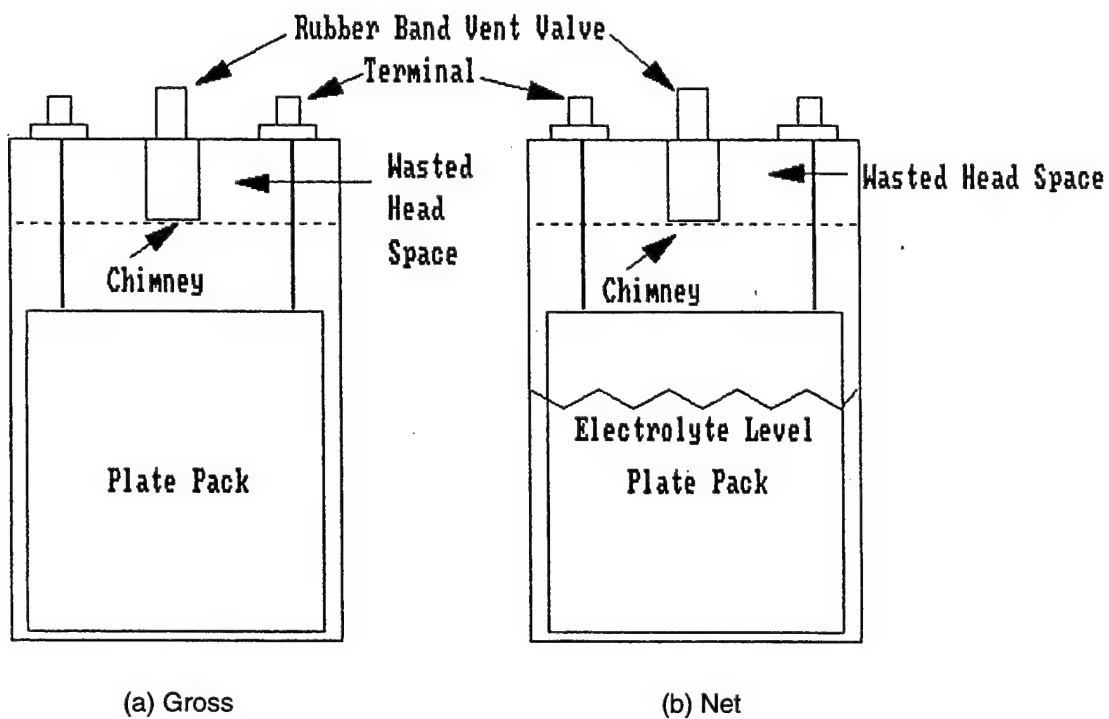


Figure 4. Interior free volume.

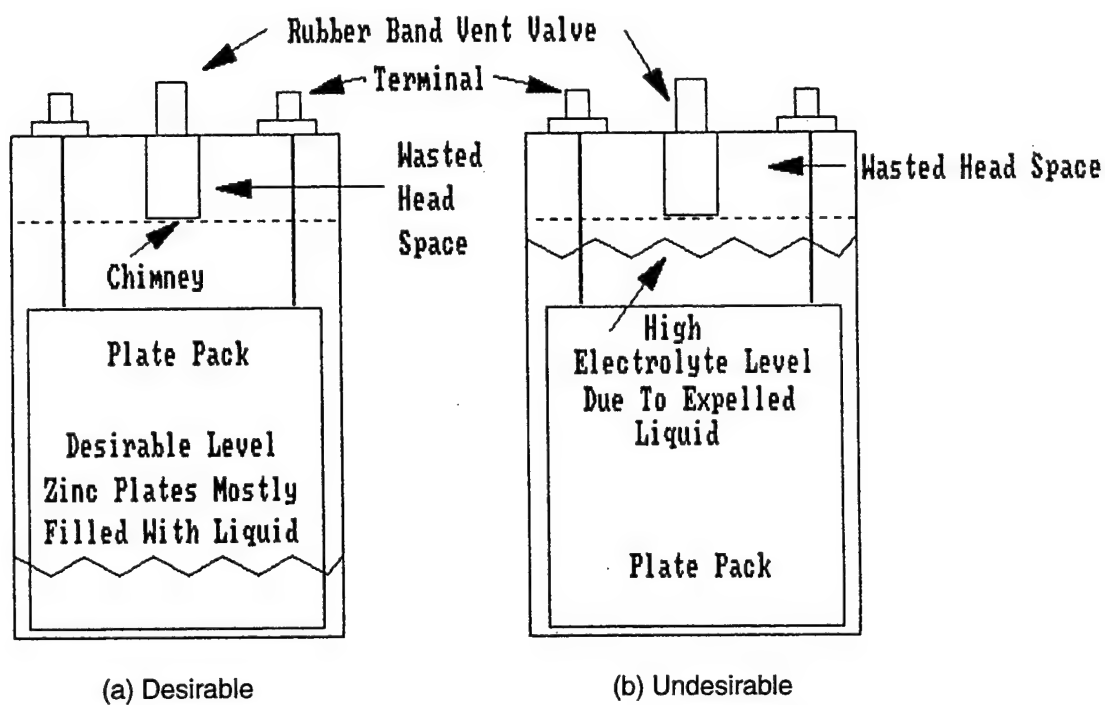


Figure 5. Electrolyte distribution.

8. Results

Our static silver-zinc model has been applied to four different cell designs. These have individual cell capacities ranging from 4.5 to 145 A-h. Table 1 gives the pertinent information stemming from the review of the internal components of these four different cell types. The information on the 10 A-h cell was gathered from a cell that had been used. These numbers are not viewed to be as accurate as those coming from unactivated cells. The other three cells had not been filled with electrolyte. All the cells were opened, and the weight, volume, and porosity of each component was measured. The Appendix contains the data gathered for a typical cell design. The manifest of internal components varies slightly from cell design to cell design so the spread sheet must be modified for each cell examined. The cell design given here as an example was a 13.5 A-h nameplate capacity cell that was used in the past by the IUS upper stage program.

The row labeled "Permissible Loss from Zinc" describes the percent of the porous volume within the zinc electrodes from which electrolyte can be expelled out into the free volume of the cell before the electrolyte level reaches the bottom of the chimney. At that point, it will be expelled from the cell. It can be seen that the 145 A-h design has a tendency to overflow to the outside of the cell if only 41% of its zinc plate porosity would contain gas instead of liquid. The 13.5 A-h design can expel up to 81% of its porous zinc volume prior to expelling electrolyte. The two smaller cell sizes can lose all of the electrolyte contained within the porous zinc plate material without any tendency to overflow electrolyte outside of the cell. A cell design very similar to the one labeled 145 A-h was involved in the IUS 13 flight, which suffered a loss of one of its batteries. This failure was believed to have been caused by the overflow of electrolyte from one or more of the cells. The free electrolyte, once outside the cells and in contact with an electrolyzing potential between the grounded battery box and the insufficiently potted cell terminals, was able to develop a destructive short circuit.

Table 1. Tolerance to Changes in Free Electrolyte Volumes of Several Cell Types

Cell Parameter (A-h)	145 (A-h)	13.5 (A-h)	10 (A-h)	4.5 (A-h)
Zinc Porosity (%)	68.7	66.5	62.7	57.5
Net Cell Interior Volume (cm ³)	359	77	57	19
Gross Free Vol (cm ³)	218	47	39	11
Net Free Vol (cm ³)	44	12	16	2.8
Minimum Free Electrolyte Vol (cm ³)	1.1	-0.7*	-4.1	2.0
Permissible Loss from Zn (%)	41	80	163**	114

*A negative number is indicative of there being less electrolyte volume than available pore volume within the components.

**A number greater than 100% is indicative of a cell design that would not be expected to overflow electrolyte under any conditions.

9. Conclusions

Electrolyte loss mechanisms associated with silver-zinc cells and batteries have been reviewed. Examples of problems in this regard have been attributed to design error of the cell, poor manufacturing quality control, inadequate activation procedures, or a combination of these factors. The efficacy of manufacturers' quality control procedures cannot be taken for granted. Cell activation procedures designed to minimize the amount of free electrolyte should be followed precisely. A static cell model has been described that focuses on electrolyte loss tendencies based on cell design in terms of available free volume coupled with the gassing characteristics of zinc electrodes. Freedom from the inadvertent loss of electrolyte was shown to be associated with proper cell designs having adequate free space within the cells. Cell designs that are subject to electrolyte loss due to inadequate free space following electrolyte addition should be reviewed, and cell case dimensions adjusted accordingly. Attempts to extend the performance or wet stand life of a battery by altering one design variable without performing a complete analysis are not recommended.

References

1. *Zinc-Silver Oxide Batteries*, edited by A. Fleischer and J. J. Lander, John Wiley & Sons, Inc.
2. Falk, S. U. and A. J. Salkind, *Alkaline Storage Batteries*, John Wiley & Sons, Inc.
3. *Handbook of Batteries and Fuel Cells*, D. Linden, Chief Editor, McGraw-Hill publishing Company.
4. Schepard, C. M. "The Silver Oxide-Zinc Alkaline Primary Cell, Part 1 Effect of Temperature and of Volume and Concentration of Electrolyte on the Relationship Between Capacity and Current Density for a Cell Using Sheet-Zinc Negative Plates," NRL Report C-3478, July 1, 1949.
5. Snyder, R. N. and J. J. Lander, "Rate of Hydrogen Evolution of Zinc Electrodes in Alkaline Solutions," *J. Electrochem. Soc.* **3**, 161 (1965).
6. Heat Sterilizable Impact Resistant Cell," ESB, Inc., Final Report, September 30, 1967 to March 31, 1970, Jet Propulsion Laboratory Contract 951296.
7. Mantell, C. L., *Electrochemical Engineering*, McGraw-Hill, 4th Edition, 1960.
8. Arcand, G. Myron, "The Reactions Pertaining to Zinc-Silver and Cadmium-Silver Batteries," Department of Chemistry, Idaho State University, Final Report, August 1, 1968, Jet Propulsion Laboratory Contract 951887.

Appendix—Silver-Zinc HR-13 Cell Design Information

1. ZINC PLATE INFORMATION

NUMBER OF FULL PLATES	9
NUMBER OF HALF PLATES	2
LENGTH-CM	8.20
WIDTH-CM	4.90
THICKNESS-.000 INCHES	22.00
WEIGHT OF HALF PLATE-GM	3.65
WEIGHT OF FULL PLATE-GM	5.70
DENSITY OF ZINC-GM/CC	7.14
GROSS VOLUME OF FULL PLATE-CC	2.25
ATOMIC WEIGHT-GM/MOL	65.40
VOLUME OF ZINC-CC	0.56
SOLID VOLUME OF FULL ZINC PLATE-CC	0.75
PLATE POROSITY-%	66.54
SOLIDS IN ALL ZINC PLATES-CC	7.70
PERCENTAGE OF PORES FILLED-%	100

2. ZINC SUBSTRATE INFORMATION

NUMBER OF SHEETS	11
LENGTH-CM	8.20
WIDTH-CM	4.90
THICKNESS-.000 INCHES	1.22
PERCENT AREA-%	95.00
WEIGHT OF SHEET-GM	1.70
DENSITY OF COPPER- GM/CC	8.92
ATOMIC WEIGHT OF COPPER	63.50
VOLUME OF SHEET-CC	0.19

3. SILVER ELECTRODE

NUMBER OF ELECTRODES	10
LENGTH-CM	8.00
WIDTH-CM	4.90
WEIGHT-GM	6.73
THICKNESS-.000 INCHES	13.00
ATOMIC WEIGHT AG	107.90
MOL WEIGHT Ag ₂ O	123.90
MOL WEIGHT AgO	231.80
DENSITY OF Ag ₂ O-GM/CC	7.14
DENSITY OF AgO-GM/CC	7.44
DENSITY OF AG	10.50
PERCENT AgO-%	
GROSS VOLUME OF PLATE	1.29
VOLUME OF AgO	0.79
SOLID VOLUME IN ELECTRODE	0.87
POROSITY OF ELECTRODE	32.71
TOTAL NEGATIVE PLATE VOLUME-CC	8.71
PERCENTAGE OF PORES FILLED-%	100

4. SILVER SUBSTRATE

NUMBER	10
--------	----

MATERIAL	SILVER
WEIGHT/PLATE-GM	0.850
DENSITY-GM/CC	10.500
VOLUME-CC	0.081
VOLUME, TOTAL-CC	0.810
5. SEPARATOR MATERIALS	
a. CELLOPHANE SHEET	
NUMBER	5
LENGTH-CM	40.70
WIDTH-CM	18.00
THICKNESS-.000 INCHES	1.50
WEIGHT-GM	2.95
DENSITY-GM/CC	1.60
TOTAL VOLUME-CC	9.22
VOLUME (DIMENSIONS)-CC	8.72
b. NONWOVEN SHEET	
NUMBER	20
LENGTH-CM	8.20
WIDTH-CM	4.90
THICKNESS-.000 INCHES	2.00
WEIGHT-GM	0.06
DENSITY-GM/CC	1.60
VOLUME, TOTAL-CC	0.69
c. NYLON MATERIAL	
NUMBER	5
LENGTH-CM	17.70
WIDTH-CM	11.50
THICKNESS-.000 INCHES	2.50
WEIGHT-GM	0.57
DENSITY-GM/CC	1.14
VOLUME, TOTAL-CC	2.50
GROSS VOLUME-CC	6.46
POROSITY-%	61.32
d. SIDE BUMPER	
NUMBER	2
LENGTH-CM	8.80
WIDTH-CM	1.50
THICKNESS-.000 INCHES	20.00
WEIGHT-GM	0.14
DENSITY-GM/CC	1.20
GROSS VOLUME-CC	1.34
VOLUME-CC	0.23
POROSITY-%	82.60
6. MISS. CELL PARTS	
a. HOLDDOWN	
WEIGHT-GM	0.73
MATERIAL	
DENSITY-GM/CC	1.5
VOLUME-CC	0.487

b. WIRES	
NUMBER	63
DIAMETER-.000 INCHES	16
LENGTH-CM	2
MATERIAL	SILVER
WEIGHT-GM EACH	
DENSITY-GM/CC	10.5
VOLUME	0.062
OVERALL CELL INFORMATION	
WEIGHT, DRY-GM	210.2
WEIGHT OF ELECTROLYTE-GM	48.3
CONCENTRATION OF ELECT.-%	42
VOLUME OF ELECTROLYTE-CC	35.0
NOMINAL CAPACITY-AHr	13.5
TYPICAL CAPACITY-AHr	15
INSIDE WIDTH-CM	1.6
INSIDE HEIGHT-CM	10.0
INSIDE BREADTH-CM	5.4
STANDPIPE DIMENSIONS	
O.D.-CM	0.80
I.D.-CM	0.40
HEIGHT-CM	0.60
VOLUME-CC	0.23
SOLID VOLUMES	
VOLUME OF NEGATIVES-CC	7.70
VOLUME OF POSITIVES-CC	8.71
VOLUME OF CELLOPHANE-CC	9.22
VOLUME OF NYLON-CC	2.50
VOLUME OF NONWOVEN-CC	0.69
VOLUME OF SIDE BUMPER-CC	1.34
VOLUME OF WIRES-CC	0.06
VOLUME OF STANDPIPE-CC	0.23
VOLUME OF HOLDDOWN-CC	0.49
TOTAL SOLID VOLUME WITHIN CELL-CC	30.94
CALCULATION OF INTERIOR FREE VOLUME	
GROSS INTERIOR CELL VOLUME-CC	85.60
WASTED VOLUME IN HEAD SPACE-CC	8.33
NET INTERIOR CELL VOLUME-CC	77.27
VOLUME OCCUPIED BY PLATE PACK-CC	30.22
GROSS INTERIOR FREE VOLUME-CC	47.04
VOLUME OF ELECTROLYTE-CC	35.00
NET INTERIOR FREE VOLUME-CC	12.04
COMPONENTS OF POROUS VOLUME	
IN NEGATIVES-CC	14.94
IN POSITIVES-CC	4.23
IN NYLON-CC	3.96
IN BUMPERS	1.11
IN CELLOPHANE-CC (swells .001.0")	9.30

IN NONWOVEN-CC	2.12
TOTAL VOLUME POROUS TO ELECT.-CC	35.66
VOLUME OF ELECTROLYTE-CC	35.00
FREE ELECTROLYTE AT 100% FILL-CC	-0.66
SPEWAGE WHEN ZINC PLATES EMPTY-CC	2.90
PERMISSIBLE VOLUME RELEASE FROM ZINC-	80.6

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and composites; development and analysis of advanced materials processing and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; spacecraft structural mechanics, space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena; microengineering technology and microinstrument development.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.